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Title: Synthesis of Hybrid Conducting Nanowire Using AAO Template

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14. ABSTRACT
The most promising way to prepare uniform dimension of nanomaterials is to use anodized alumina membrane as template. The work emphasized self-organized arrangement of pores in hexagonal array and vertical direction expansion for the high aspect ratio, and the self-liming surface reaction. From these approaches, the atomic layer deposition was controlled precisely at the molecular level.

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1. Introcduction

A number of ways for the synthesis of nanomaterials have been reported previously, since the discovery of carbon nanotube in 1991. It has been a great challenge to develop fabrication technology of nanomaterials such as nanotubes and nanowires in regular arrangement. With decreasing size of diameter in nanoscale, the corresponding increase of nanomaterial density appears and the totally different features from the solid or two-dimensional structures are observed. Especially one dimensional nanostructures of various metal or semiconductors offer unusual novel quantum phenomena in the limit of small diameter and its potential use in electronics, photonics, and sensors attracts much attention for the application of diversified nanodevices. In addition, much more efforts have been made to focus on the synthesis of nanomaterials in uniform dimension and it would open up the new opportunity to test the concept of nanobuilding block to the electrical, optical, and mechanical applications.

The most promising way to prepare uniform dimension of nanomaterials is to use anodized alumina membrane as template. Self-organized arrangement of pores in hexagonal array occurs due to repulsive interaction between pores and vertical upward direction of expansion at the entire bottom and existing pore walls preparation of high aspect ratio template. With pore diameters in the range of 20 nm to about 400 nm and maximum pore length of couple of 100 micron, the perfected ordered structure of high aspect ratio template can be fabricated up to more than 10000. The regular dimension of pores in the alumina template can be controlled by manipulating the anodization parameters and it would enable to fabricate nanomaterials of uniform dimension, such as carbon nanotube, nanowire of metal or metal oxide in the confined geometry of template. However, the limitation of anodization process in the electrochemical procedure prevents the pore formation of alumina template less than 10 nm diameter. There is couple of methods to reduce the pore diameter of alumina template, such as surface layer deposition with inorganic materials, atomic layer deposition of metal oxide, ion beam sculpting of alumina template, and optimization of anodization parameters. Among these four possible methods, uniform reduction of pore dimension is very critical for the preparation of nanomaterial and atomic layer deposition seems to be the most efficcient technique to control the deposition layer thickness. The atomic layer deposition of thin film is to use the self-limiting surface reactions applied in a binary reaction sequence and it allows us to control the deposition of full monolayer every adsorption cycle. Each surface reaction occurs between a gas phase reactant and a surface functional group and the functionality on the surface changes from one species to another. The overall reaction for Al_2O_3 deposition is $2Al(CH_3)_3 + 3H_2O$ ------>$Al_2O_3 + 6CH_4$ and the binary reaction sequence is divided into two half reactions,

(A) $AlOH^* + Al(CH_3)_3 \longrightarrow Al\text{-}O\text{-}Al(CH_3)_2^* + CH_4$

(B) $AlCH_3^* + H_2O \longrightarrow AlOH^* + CH_4$

where the asterisks represent the surface species.

Using ZnO as atomic layer deposition, the overall sequence chemistry for the monolayer growth is Zn(CH2CH3)2 + H2O --------->> ZnO + 2CH3CH3. This binary reaction consists of consecutive exposure of diethyl zinc and H_2O alternatively and it can be divided into the two half-reactions:

(A) $ZnOH^* + Zn(CH_2CH_3)_2 \longrightarrow Zn\text{-}O\text{-}Zn(CH_2CH_3)^* + CH_3CH_3$

(B) $Zn(CH_2CH_3)^* + H_2O \longrightarrow ZnOH^* + CH_3CH_3$

From the self-limiting surface reaction of these precursors, atomic layer deposition can be controlled very precisely as molecular level.

Here, we present the results of atomic layer deposition of zinc oxide and alujminum oxide in anodized aluminum oxide (AAO) template with various aspect ratio and structural features. The potential new approach to synthesize single wall carbon nanotube with uniform dimension and defect-free structure will be discussed. To achieve the better understanding of the physical properties of nanomaterials, it is important to develop fabrication technology of nanostructures with controlled dimension. Besides, for the preparation of single wall carbon nanotube, it is mandatory to prepare the pore diameter less than 3 nm.

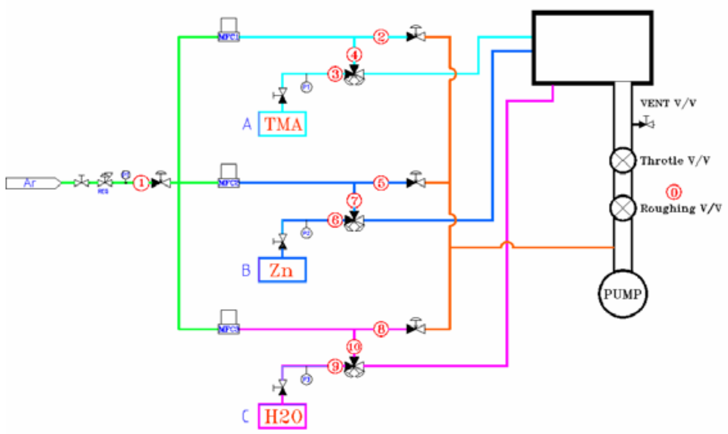
2. Experimentals

Anodized aluminum oxide (AAO) template was prepared from 99.999% purity aluminum foil by performing the following steps in sequence; aluminum plate washing and preparation, aluminum plate electropolishing, first anodizing, etching, second anodizing, pore widening. By varying the process parameters such as anodizing solution concentration, anodizing temperature, anodizing time, reaction gas composition, and size of catalyst, the dimension of the pores in AAO template can be manipulated according to the application purpose. High purity aluminum foil was electropolished in a mixed solution of perchloric acid and ethanol at 7 C for 2 minutes, followed by washing in ethanol and deionized water three times. First anodization has been done in 0.3 M oxalic acid at 17 C and DC 25 V for 12 hours and the anodized layer of alumina was etched away in chromium oxide solution at 65 C for 3 hours. For the desired thickness of anodized alumina layer, the second anodization was performed using the same condition but different anodization time which allows various length of alumina template. Pore widening was

done in 0.1 M phosphoric acid for 50 minutes and AAO template of out 85 nm diameter of pore is expected.

The depositions of ZnO and Al_2O_3 component on the AAO (Anodized Aluminumoxide) template were performed by the atomic-layer-deposition (ALD) technique using traveling-wave type ALD reactor (Ever-tek. Co, Plus-100). As the precursors of ZnO and Al_2O_3 layer deposition, diethyl zinc (DEZ, $Zn(C_2H_5)_2$) and trimethyl aluminium (TMA, $Al(CH_3)_3$)) were used respectively and H_2O was used as the oxidant. At first, Al_2O_3 was deposited inside the pore of anodized alumina template with pore diameter of 85 nm and pore length of 2.5 μm. The alumina template was cleaned in 30% H_2O_2 solution and placed in the sample holder of atomic layer deposition chamber. The sample temperature was maintained at 180 during the deposition. The chamber was pumped down to < 1 X 10^{-5} Torr before the TMA exposure and TMA and H_2O were pumped alternatively. Finally the deposition chamber was pumped with diffusion pump for 2 minutes.

Figure 1. Schematic Diagram of Atomic Layer Deposition System



For the deposition of ZnO, the atomic layer deposition was also made inside pore of alumina template which has the pore diameter of 85 nm and pore length of 2.5 μm. Sequence chemistry consisting of 0.5 sec DEZ pulse / 12 sec Ar purge / 0.5 s H_2O pulse / 23 sec Ar purge was preformed 110 cycle consecutively. The rather long Ar purge time was adopted to guarantee good conformality of the films over the tiny holes.

The alumina template before and after atomic layer deposition were characterized by high resolution FE-SEM(Hitachi S-5200).

3. Results and Discussion

From the two-step anodization process, highly ordered domains of alumina template with hexagonal order were prepared by varying the second anodization time and pore widening time. As seen in Figure 2-a, the hexagonally ordered pore arrays were produced by two-step anodization at 25 V in 0.3 M oxalic acid solution followed by pore widening in 0.1 M phosphoric acid for 50 minutes. The average pore diameter and interpore distance are 85 nm and 120 nm respectively. By changing the pore widening time from 10 to 50 minutes, the pore diameter of template were widened from 25 nm t0 85 nm (Figure 2-b). Usually the interpore distance of 50, 60, 100, 150, and 420 nm corresponds to the pore density range of 6 X 10^8 to 5 X 10^{10} cm^{-2} and interpore distance of 120 nm in Figure 2 has the pore density of 7 X 10^9 cm^{-2}. Second anodization at 25 V in oxalic acid solution for 20 minutes gives pore length of 2.5 μm as seen in Figure 3-a. With increasing anodizing time from 5 to 20 minutes, the pore length of more than 3 μm can be manipulated. Depending upon the diameter and length of pore dimension inside the alumina template, it would have the different aspect ratio which affects the surface reaction during the atomic layer deposition.

The atomic layer deposition conditions for TMA and H_2O half-reactions on the surface of porous alumina template were studied using several reaction parameters such as reactant precursors inlet time, Ar purge time, and reaction temperature. The atomic layer deposition of Al_2O_3 was performed 200 and 350 cycles using sequence chemistry consisting of 0.2 sec TMA pulse / 10 sec Ar purge / 0.5 sec Al_2O_3 pulse/ 30 sec Ar purge subsequently. Anodized alumina template with 85 nm diameter and 2.5 μm length was used. By comparing the surface morphology inside the pore of alumina template before and after atomic layer deposition, the surface chemistry on the alumina pore as well as Al_2O_3 deposition rate were studied using TMA and H_2O precursors.

For the half-reaction in the binary chemistry of Al_2O_3 deposition, the most important feature is the number of AB cycles which is directly proportional to the deposition film thickness. Since the number of the reactive sites on the flat surface of Al_2O_3 is considered to be constant during the monolayer deposition, it gives almost constant deposition rate per each cycle. However, the surface geometry, the substrate characteristics, and pumping efficiency in the CVD chamber would be the variable parameters which affect the deposition morphology especially for very narrow pore diameter.

After 200 cycles of TMA and H_2O half-reactions, the pore diameter of alumina template was reduced down from 85 nm to 18 nm as seen in Figure 4-a. It was found that the uniform reduction of the pore diameters around the mouth of the alumina template was obtained. Figure 4-b shows that pore diameter has been reduced to 7 nm very evenly after 325 cycles. Even though atomic layer deposition is useful for the processing of metal oxide, it might have the

limitation especially for the application of very small diameter or high aspect ratio. In order to identify the uniform deposition along the pore channel, the alumina specimen was fractured and both cross-section and top surface was observed by FE SEM.

The micromorphology of AAO template before and after atomic layer deposition (ALD) of ZnO was studied by SEM. Figure 5-a shows that ZnO has been deposited to reduce the diameter from 70 nm to 18 nm. Besides the inner channel of the alumina template exhibits the uniform channel diameter of 18 nm down to bottom of the pore by depositing ZnO as shown in figure 5-b. Therefore, it can be said that the pore dimension of AAO template can be successfully reduced by atomic layer deposition of Zno and Al_2O_3 . It also shows high potential that single wall carbon nanotube can be synthesized by utilizing ALD method to prepare the AAO template less than 3 nm.

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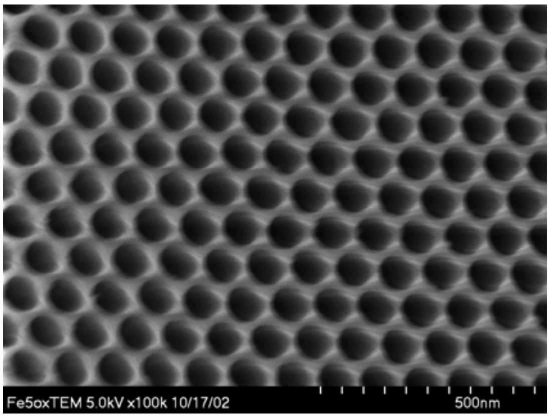
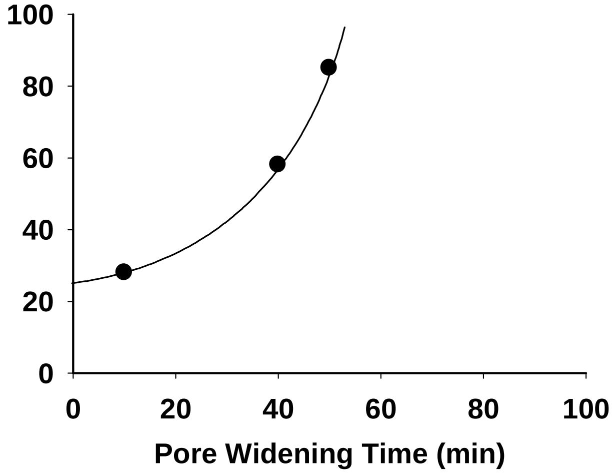
Figure 2. Hexagonally ordered pore array of AAO template (a), Pore diameter variation of AAO template as a function of pore widening time (b)



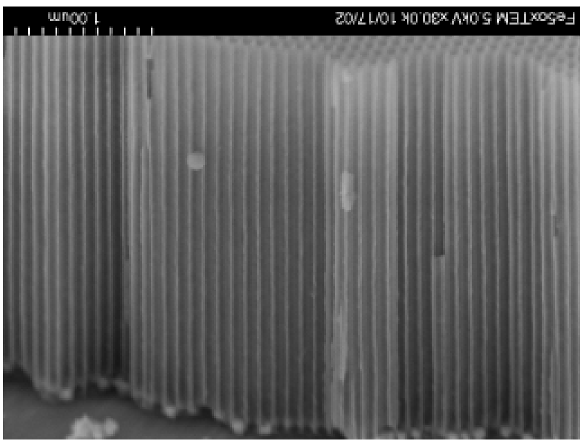
(a)



(b)

Figure 3. Fracture surface of pore along the channel (a), Pore length of AAO template as a function of anodization time (b)

(a)



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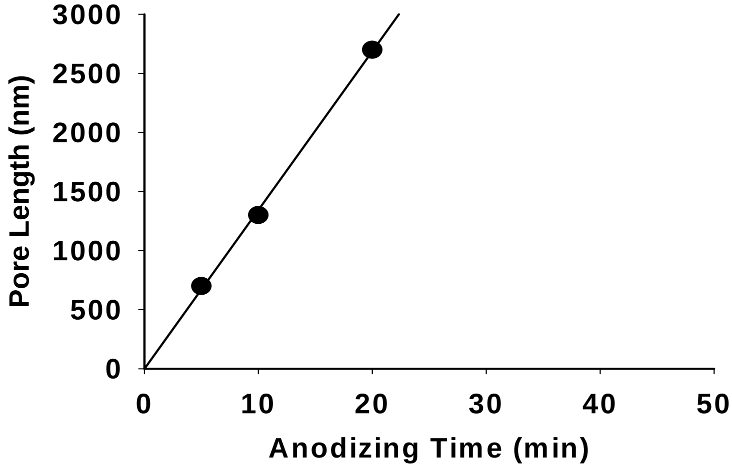

Pore Length (nm)
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
Anodizing Time (min)